

## ORIGINAL RESEARCH PAPER

**Investigation of photocatalytic degradation of clindamycin by TiO<sub>2</sub>****Azam Gholami, Mahmood Hajiani\*, Mohammad Hossein Sayadi Anari***Department of Environmental Engineering, Faculty of Natural Resources and Environment, University of Birjand, Iran*

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**ABSTRACT**

Contaminants of emerging concern or simply emerging contaminants have been considered as a critical environmental issue in recent decades. These compounds have not routinely controlled and monitored; therefore they have posed risk to the health of human and environment. Drugs are considered as one of the most important emerging pollutants. They introduce to environment from different sources such as urine, human excretion, livestock, poultry, pharmaceutical, and hospitals. Although they are in trace levels, they are not biodegradable. They cannot be removed by conventional treatment processes. Advanced oxidation processes (AOPs) have been designed to address the deficiency of conventional methods in the removal of emerging pollutants. Production of highly reactive hydroxyl radicals is the base of AOPs. These very reactive radicals effectively oxidize emerging pollutants such as drugs. Among different approach of AOPs, photocatalytic degradation has been successfully applied to mitigate the side effects of emerging contaminants. The ability of the photocatalytic process in the removal of Clindamycin hydrochloride (CLM) from aqueous solutions in the presence of UV/TiO<sub>2</sub> was studied. The effects of various parameters such as adsorption, photolysis, pH, catalyst dosage, initial concentration of antibiotic, and radiation time were investigated in a batch photoreactor. Results showed that photolysis and adsorption had a negligible contribution to the clindamycin removal. The maximum clindamycin removal rate was obtained under optimal conditions, such as pH of 5, 0.5 g/l of TiO<sub>2</sub>, initial clindamycin concentration of 2 /L. This optimum condition was achieved for 90 minutes. The CLM photocatalytic degradation kinetics showed that CLM degradation follows the pseudo-first-order kinetics.

**Keywords:** *Advanced Oxidation Process, Emerging Pollutants, Titanium Dioxide***How to cite this article**

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**INTRODUCTION**

Among the various compounds that cause environmental pollution, residual drugs in wastewater pose serious environmental issues. They are considered as emerging pollutants [1, 2]. Although many works have been made to clean the environment from pollutants in recent decades, emerging pollutants have been disregarded [3, 4]. While the pathway of general pollutants in the environment is under control and monitoring, the fate of emerging pollutants is not clear. Lacks of environmental legislation and weakness of conventional methods in the removal of drugs

lead to concern in scientific communities [2, 4-7]. Although the emerging pollutants in wastewater might be in trace levels, bioaccumulation of drugs in the environment have threatened human health and consequently posed potential hazards to ecosystems [2, 8]. Among different types of drugs, antibiotics are frequently consumed by human, livestock and poultry industries. Antibiotics are used as an effective drug against bacteria, fungi, infections and all types of parasites. Increasing rates of using antibiotics led to the release of a high amount of these types of drugs to environments. Their introduction into the environment can lead

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to reducing bio-degradation of organic matter in nature, including leaves and other plant materials. They aren't biodegradable, consequently, antibiotic-resistant bacteria (ARB) and antibiotic resistance genes (ARG) are other concerns [9-12]. Therefore, the removal efficiency of conventional methods for these contaminants doesn't meet the standard criteria. The deficiency of conventional wastewater treatments leads to some robust technique such as advanced oxidation processes (AOPs)[13].

AOPs are environmental friendly approaches based on producing hydroxyl ( $\text{OH}^\bullet$ ) and superoxide ( $\text{O}^\bullet$ ) radicals. These radicals destroy pollutants and organic matters non-selectively. Different approaches of AOPs have been applied to remove antibiotics [17-19]. For example, amoxicillin, ampicillin, atenolol, and caffeine could be removed using Photolysis, ozonation, ozonation with UV radiation, homogeneous catalytic ozonation[18]. The ozonation process has extensively applied in a variety of studies to remove indomethacin[20], propranolol [21], tetracycline [22], Carbamazepine, diclofenac, sulfamethoxazole, and trimethoprim [23], Ibuprofen, acetyl sulfamethoxazole and metoprolol[24]. The efficiency of UV/H<sub>2</sub>O<sub>2</sub> and UV were examined for removal of Sulfamethoxazole, sulfamethazine, sulfadiazine, trimethoprim [25], Sulfasalazine, sulfapyridine and 5-aminosalicylic acid [26], azithromycin, carbamazepine, dexamethasone, erythromycin, and oxytetracycline[27], Sulfamethoxazole and ibuprofen[28]. Diclofenac, sulfamethoxazole, iopromide, and 17- $\alpha$ -ethinyl estradiol were removed using Electrochemical oxidation[29]. Ultrasound/Fenton oxidation (sonoFenton) degraded Ibuprofen[30]. Degradation of Venlafaxine was investigated by Electro-peroxone process[31]. Among the advanced oxidation processes, the semiconductor heterogeneous photocatalytic process has high efficiency in the decomposition of organic compounds resistant to biotic degradation [32-34]. The main focus of researches has been on the application of semiconductor in the removal of drugs and other pollutants from the environment[35]. Having photostability and ability to readily oxidize both organic and inorganic matters, has made a fundamental role for TiO<sub>2</sub> since the origin of the photodegradation process[36]. Having a considerable bandgap, in the rutile (bandgap 3.0 eV) and anatase (bandgap 3.2 eV) phases, TiO<sub>2</sub> has been widely used in different aspect of science [35,

37]. A combination of 25% and 75% in the rutile and anatase phases, respectively, have been used successfully in the removal of emerging pollutants [38,39]. So far, many semiconductors have been investigated as photocatalyst but TiO<sub>2</sub> is still used as the most widely used photocatalyst due to its properties such as chemical and photochemical stability, abundance, low cost, and high optical activity. In addition, other semiconductors, such as ZnO, CdS and GaP, cannot be cleaned from the environment due to the solubility and production of toxic products [2,40]

Clindamycin is a lincosamide antibiotic which is very effective against gram-positive and negative anaerobic pathogens as well as aerobic microbes. This antibiotic can destroy them by inhibiting the synthesis of bacterial proteins [41]. Although Clindamycin has side effects such as anaphylaxis, polyarthrititis, hepatotoxicity, and diarrhea Clindamycin is widely used orally (hydrochloride salt), intravenously (phosphate salt) and topically. Therefore, it can be introduced to wastewater through urine and human excretion, and the destruction of expired drugs [42, 43]. Consequently, the presence of Clindamycin in wastewater could result in ARB [44].

Using moving bed biofilm reactors have been removed Clindamycin from the effluent of conventional wastewater treatment plant [43]. The sorption method by two surfactant-modified zeolitic tuffs was showed the removal of Clindamycin between 12 and 15 hours [44]. Nanoscale zero-valent iron (nZVI) particles in the presence of hydrogen peroxide and sonolysis were used to degrade Clindamycin. The process showed that the combined system was more efficient in the removal of Clindamycin [45]. Clindamycin was degraded in aqueous solutions using an anodic oxidation process under galvanostatic conditions. Ti/SnO<sub>2</sub>-Sb anode and a 316 stainless steel cathode made electrolysis cells [46]. Using ZnO as photocatalyst in a batch reactor, Clindamycin was removed from aqueous solutions [47]. Using TiO<sub>2</sub> as a semiconductor photocatalyst, removal of Clindamycin was investigated under UV radiation in aqueous solutions. Experiments were conducted under different conditions of pH. Moreover, the effects of some parameters such as initial concentrations of Clindamycin, catalyst dose, radiation time were studied. The degradation rate of antibiotic was investigated by measuring the kinetics of the reaction.

## EXPERIMENTS

### Materials

Titanium dioxide ( $\text{TiO}_2$ ) with a purity of 99.5% produced by DEGUSSA Co. was used in this study. Analyzes such as X-ray diffraction analysis XRD (X'Pert Pro, PANalytical, Holland) in the scanning range ( $2\theta$ ) of  $10\text{--}80^\circ$ , Transmission electron microscopy TEM (CM120, Philips, Holland) at an accelerating voltage of 120kV, and Fourier transform infrared spectrometer FT-IR (IRAffinity-1S, Shimadzu, Japan) has been used to determine the specifications of  $\text{TiO}_2$ . Clindamycin HCl ( $\text{C}_{18}\text{H}_{33}\text{ClN}_2\text{O}_5\text{S}\cdot\text{HCl}$ ) Antibiotic was prepared from the Sigma Aldrich Co. Other chemicals were purchased from the Merc Co. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) 1N were used to adjust the pH. Cyclohexane ( $\text{C}_6\text{H}_{12}$ ), potassium iodide ( $\text{KIO}_3$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) 95% were used to analyze the samples.

### Photoreactor

Fig. 1 shows the photoreactor used for experiments. This photoreactor was a 1000 ml metallic cylinder. Three UV-C lamps were used as sources of radiation. The distance between each lamp was the same and equal to radiate uniformly to the samples. Direct contact between lamps and solution was prevented by coating the lamp in a quartz tube. Samples were homogeneous using an air pump. Sampling was carried out through an outlet at the top of the reactor.

### Photocatalytic experiments

The samples consisted of a solution containing a specific concentration of Clindamycin. To make homogeneous solutions, samples were placed on the shaker for 15 minutes.  $\text{TiO}_2$  was added to the solution and stirred using a magnetic stirrer to mix. Ultrasonic bath for 15 minutes was used to prevent aggregation of  $\text{TiO}_2$ . pH was adjusted using HCl and NaOH. Prepared samples were then poured into the photoreactor and aeration was conducted by an air pump. From this moment on which is the beginning of the photocatalytic reaction, sampling was performed at specified intervals. At each sampling 5 ml of solution was extracted from the photoreactor. After the reaction, the centrifuge was used at 2000 rpm for 20 minutes to separate photocatalyst nanoparticles.

### Sample analysis

Sample analysis was performed by spectrophotometric. The method was based on the production of sulfone from organic sulfides. Due to methylthio group attached to sugar moiety of Clindamycin, sulfur was oxidized by using potassium iodate in an acidic environment. Liberated iodine was equivalent to oxidation of sulfur atom. Iodine was extracted in cyclohexane and measured using spectrophotometer at 520 nm [48] To apply the method Centrifuged samples were transferred to 25 ml flasks. To each flask, 3 cc of potassium iodate solution 1% and 2 cc of



Fig. 1. Photoreactor used in the experiments

sulfuric acid 30% v/v were added. Then, 10 ml of cyclohexane was added to each flask. A two different phase solution was made after adding cyclohexane. The flasks were placed in a water bath at a temperature of 60 °C. After 45 minutes, samples were removed from the water bath and placed at room temperature. Waiting to reach the room temperature, the cyclohexane layer in each flask was extracted and transferred to another 25 ml volumetric flasks. Once more, 5cc of Cyclohexane was added to the first flasks and the extraction of cyclohexane was performed after 15 minutes but at room temperature. The procedure was repeated too. Extracted cyclohexane was volume up at 25 ml by cyclohexane. The absorbance measurements were carried out at the wavelength of 520 nm against the control which was equal to Clindamycin in each flask after photodegradation. The procedure has been presented in Fig. 2.

**RESULTS AND DISCUSSION**

*Photolysis and adsorption*

To measure the amount of adsorption, experiments were conducted in darkness with

a solution containing 2 g/l of CLM and catalyst content of 1 g/l. The results showed that the absorption was negligible and only 20%. Photolysis experiments were investigated for 120 minutes. The results showed the negligible contaminant removal of about 10%.

*effect of PH*

The effect of pH on the removal of Clindamycin was investigated during 120 minutes (Fig. 3). The analyses of pH effects were examined at a pH of 5, 7, and 9. Fig. 3 shows that the maximum removal rate is achieved in acidic pH.

The pH of a solution is one of the important factors for the photocatalytic purification of organic pollutants. It has a direct impact on the efficiency of the process. The changes of pH affect the catalyst surface, the size of the catalyst clots, the solubility of the antibiotics and also the ability to produce radical hydroxyl. Moreover, the nature of the pollutant ion, which varies with the changing pH of the environment, leads to the creation of electrostatic interactions between the catalyst surface and the pollutant molecule.

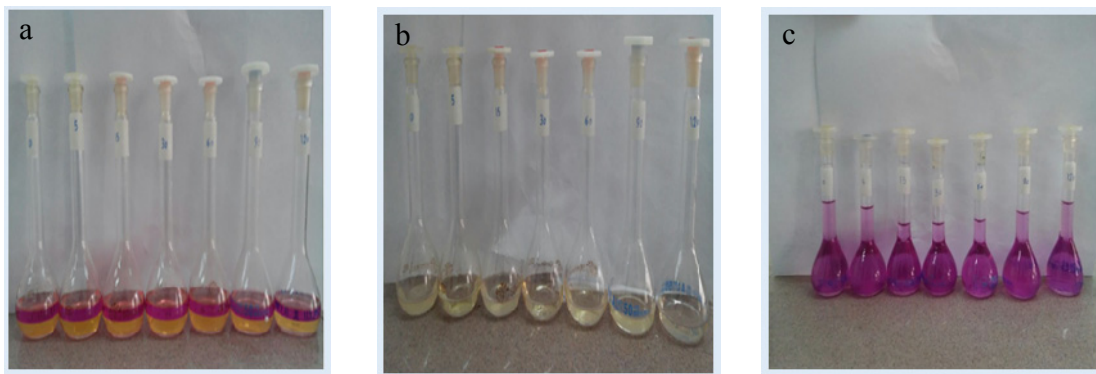


Fig. 2. Spectrophotometric and titrimetric method (a) Flasks removed from the water bath, (b) Flasks extracted from Cyclohexane and (c) Flasks volume up at 25 ml by Cyclohexane.

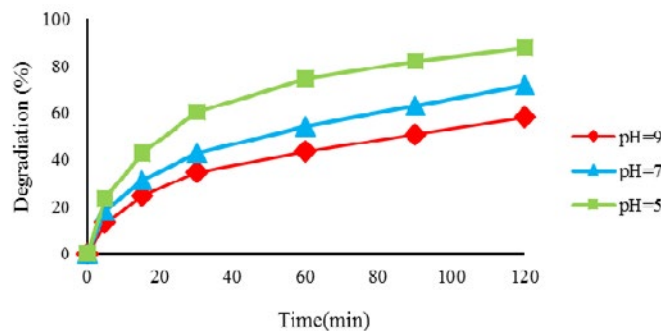


Fig. 3. Effects of pH on photocatalytic degradation of Clindamycin

Due to the high concentrations of hydrogen ions in acidic medium,  $H^{\bullet}$  radicals are formed. Ultimately, they transform into hydroxyl radicals ( $OH^{\bullet}$ ) with high degradation ability, using the oxygen present in the solution. Reducing the reaction rate in alkaline environments is due to the formation of insoluble compounds, followed by the reduction of radiation intensity. Therefore, the potential production of hydroxyl radicals is decreased [51].

*Effects of Clindamycin concentrations*

Fig. 4 shows the effect of the initial concentration of Clindamycin. By decreasing the initial concentration of antibiotic, removal rates will increase. The maximum removal rate was observed at an antibiotic concentration of 2 g/L.

Increasing the initial concentration of the pollutant leads to decreased photodegradation rate. This phenomenon occurs due to saturation or inactivity of a limited number of active sites on the catalyst surface. High concentrations of pollutants

can form intermediates. These compounds could be absorbed by the catalyst; consequently, degrade the active sites. Occupied sites are no longer able to absorb active species ( $H_2O$ ,  $OH^{\bullet}$ , and  $O_2$ ). This circumstance reduces the reaction with holes of the capacity and conduction band electrons thereby reduces the production of oxidants. Moreover, in medium with high concentrations of pollutants, lower number of photons reaches the catalyst surface which reduces the activity of optical degradation [52,53]

*Effects of catalyst concentrations*

To evaluate the effect of catalyst, different amount of  $TiO_2$  were used. The results have been presented in Fig. 5. As observed, increasing the catalyst content to a specific point increases the pollutant removal rate. However, a further increase of catalyst from that point leads to a decrease in removal rate.

Increasing catalyst content leads to increased pollutant degradation efficiency because the

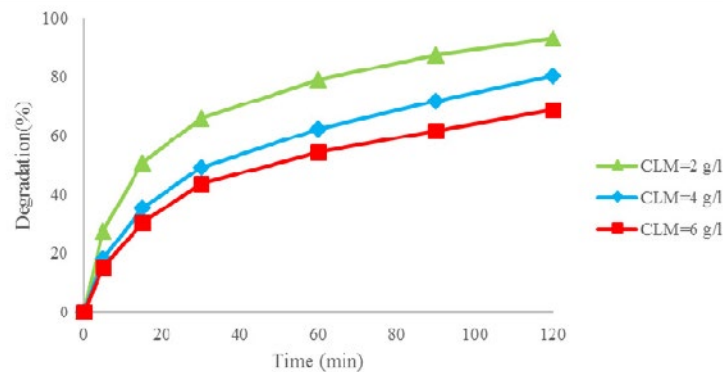


Fig. 4. Effects of Clindamycin concentration on photocatalytic degradation

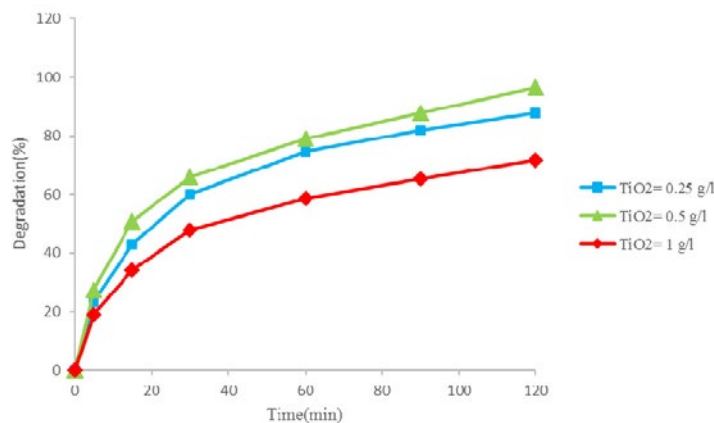


Fig. 5. Effects of Clindamycin concentration on photocatalytic degradation



number of photons absorbed increases. Absorbing more photon results in the number of active sites on the catalyst surface. Increasing the number of active sites can also play an important role in the production of hydroxyl and superoxide radicals. However, an excessive increase in catalyst content yields a drop in reaction rate. This phenomenon occurs due to increased turbidity and consequently reduced light penetration and dispersion [54].

*Effect of time*

Effects of time on the removal of the antibiotic during 120 minutes are shown in Fig. 6. results show that the removal rate was initially high. By passing the time, the reaction rate is reduced and reaches the equilibrium state.

At the beginning of the experiments, there is a large number of vacant sites on the catalyst surface. After a time, the number of these active sites decreases. In the equilibrium state, the degradation rate is stable. In the present study, stable conditions are after 90 minutes[51].

*Degradation kinetics*

The following equation was used to study the kinetics of the reaction based on regression analysis:

$$\frac{dc}{dt} = -KC$$

By integrating the equation above, the following equation is obtained:

$$\ln\left(\frac{C}{C_0}\right) = -Kt$$

Where  $K$  and  $t$  are respectively constants of reaction rate and time.  $C$  and  $C_0$  are the reactant concentrations at  $t = t$  and  $t = 0$ .

The results in optimal conditions (pH of 5 and initial concentration of Clindamycin of 2 g/l ) during 120 minute for catalyst amount of 0.25, 0.5, and 1 g/l are shown in Fig. 7. It can be observed, the degradation is in the form of a straight line. The slope of the graph represents the constant reaction rate ( $K$ ). Accordingly, it can be concluded that the photocatalytic degradation of Clindamycin follows the first-order kinetics.

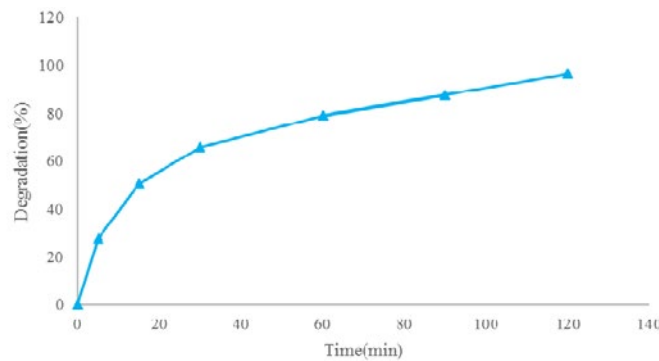


Fig. 6. Effects of Clindamycin concentration on photocatalytic degradation

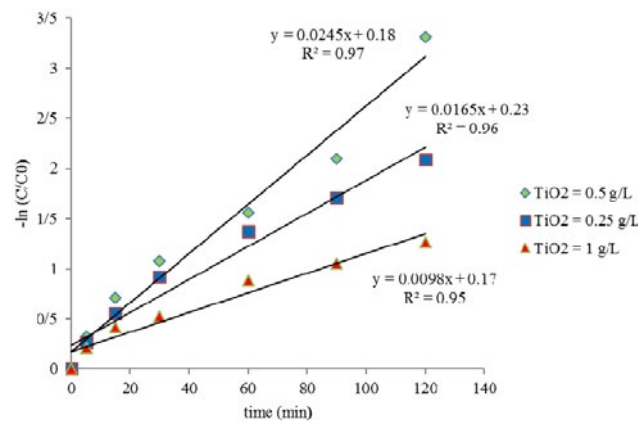


Fig. 7. Effects of TiO<sub>2</sub> amount on degradation kinetics (CLM=2 g/l,pH=5)

## CONCLUSION

Degradation of Clindamycin hydrochloride antibiotic was investigated under laboratory conditions by heterogeneous UV/TiO<sub>2</sub> process. The results showed that direct adsorption and photolysis did not affect photocatalysis. The optimum point was observed at pH = 5, Clindamycin concentration of 2 g/L, catalyst amount of 0.5 g/l, during 90 minutes. The degradation kinetics follow the pseudo-first-order. The results of this study prove that the UV/TiO<sub>2</sub> process is a very effective method in removal of Clindamycin hydrochloride from the aqueous medium.

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## CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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